

New iron polyoxometalate - based catalysts for decontamination of HD and G agents

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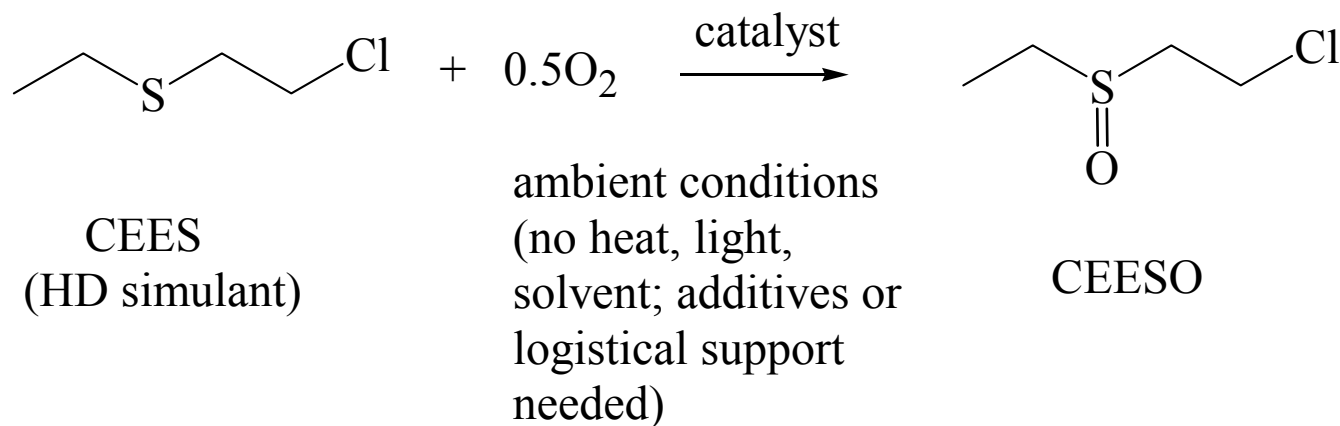
Outline of today's talk

- Iron containing POMs.
- Iron POM with terminally coordinate redox-active ligand and the catalytic activity of this conjugate complex.
- Cationic silica nanoparticles " $\text{Si}/\text{AlO}_2^{n+}$ ".
- Electrostatic binding of iron POMs to $\text{Si}/\text{AlO}_2^{n+}$.
- Catalytic activity of iron POMs bound to $\text{Si}/\text{AlO}_2^{n+}$.

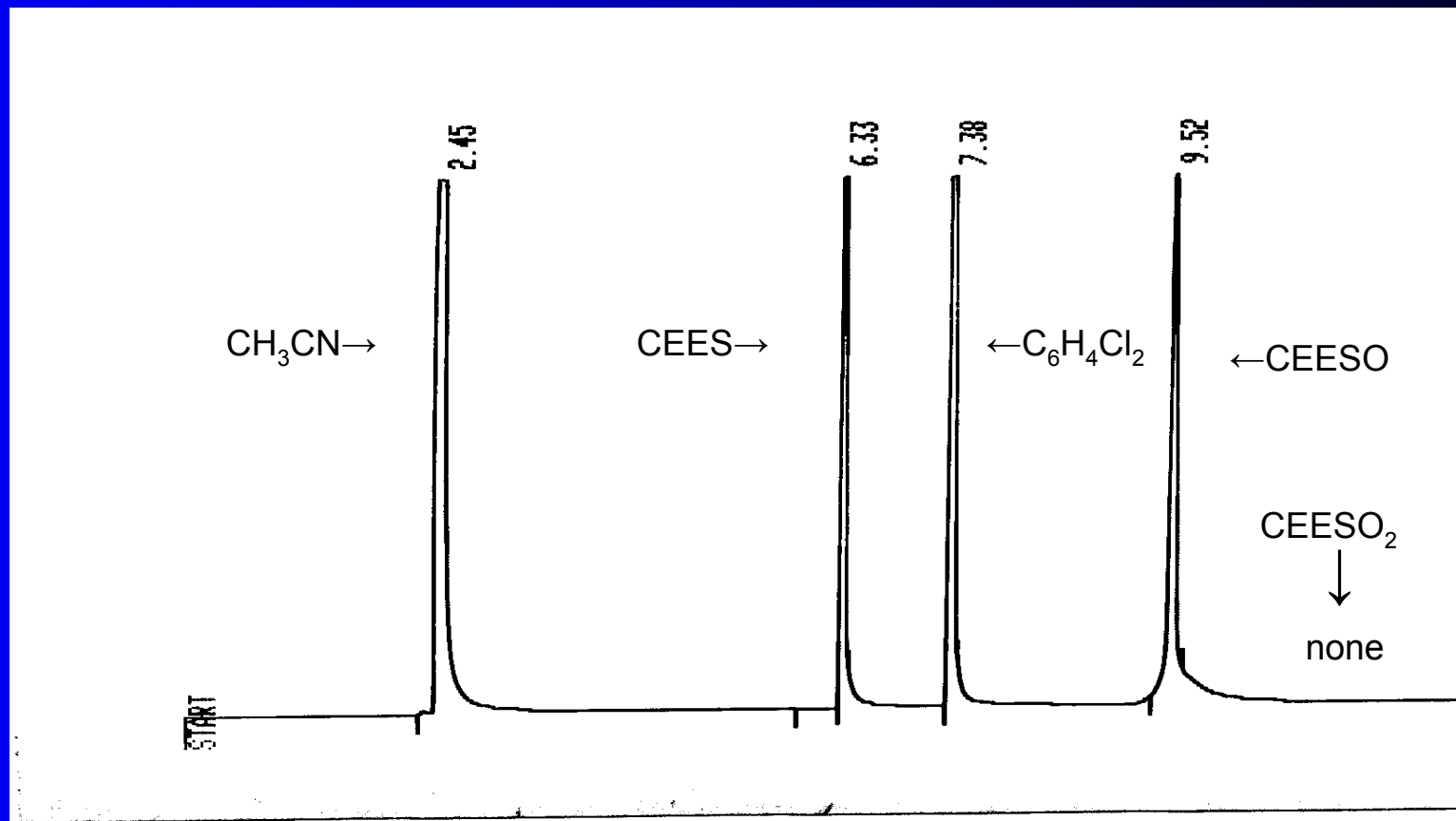
New iron containing POMs

Recently developed iron containing polyoxometalates (POMs) are the most reactive catalysts yet for the rapid aerobic oxidation/ decontamination of mustard (HD) and the optimal simulant for HD, 2-chlorethyl ethyl sulfide, CEES. Only the ambient environment is required (air at room temperature). Turnover rates are high, selectivity to the desired sulfoxide is ~100%, and the most recent catalyst is very stable.

Exemplary reaction (stoichiometry, conditions)

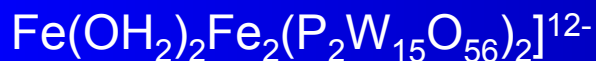
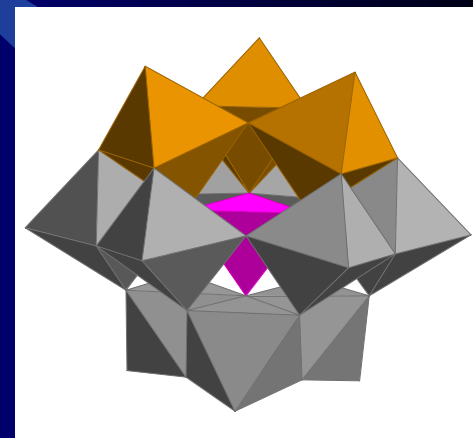
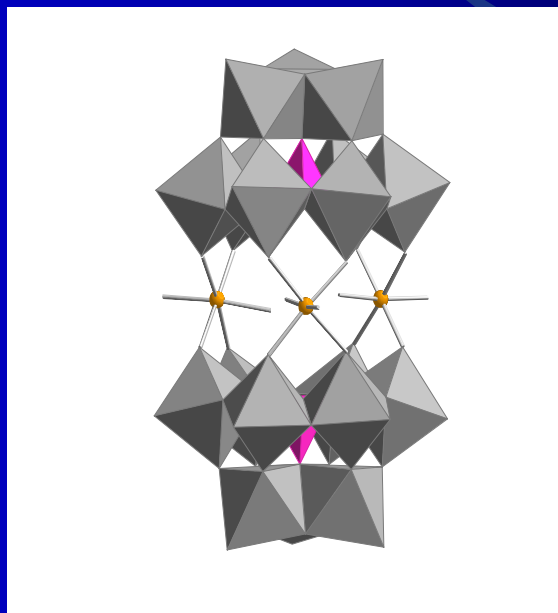
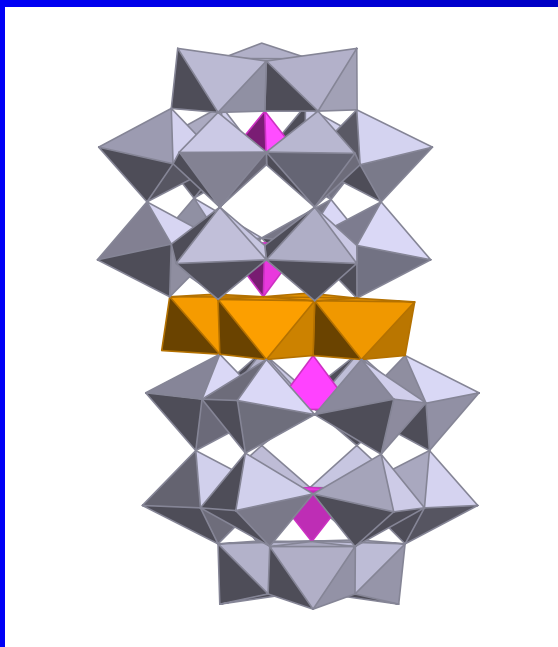


Quantitative selectivity for minimally toxic sulfoxide product



Conversions in all cases ultimately approach 100% also

Structures of recent catalytically active iron containing POMs

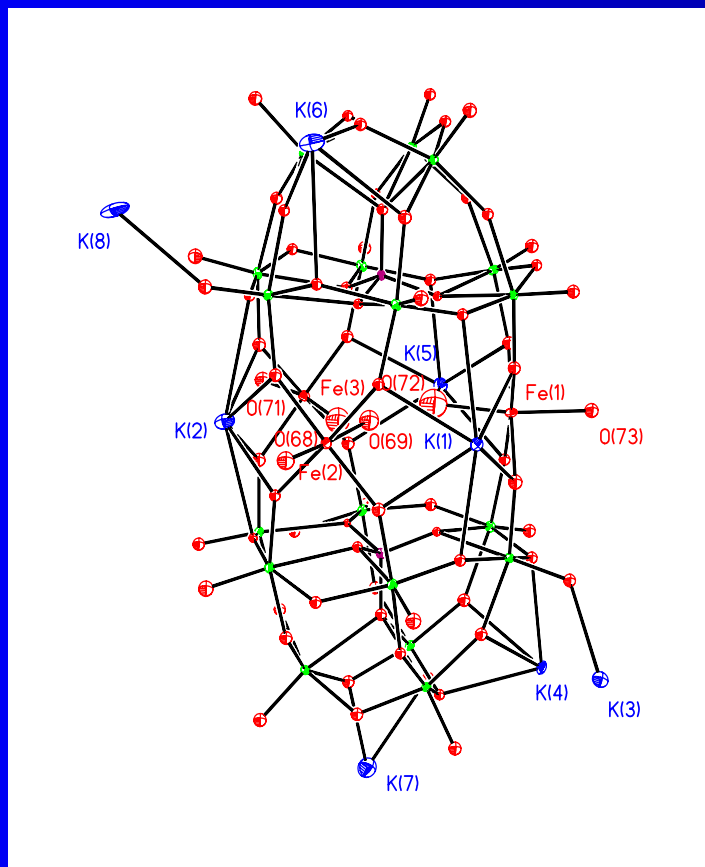


T.M. Anderson, X. Zang, K.A. Hardcastle, C.L. Hill, *Inorg. Chem.* **2002**, 41, 2477 .

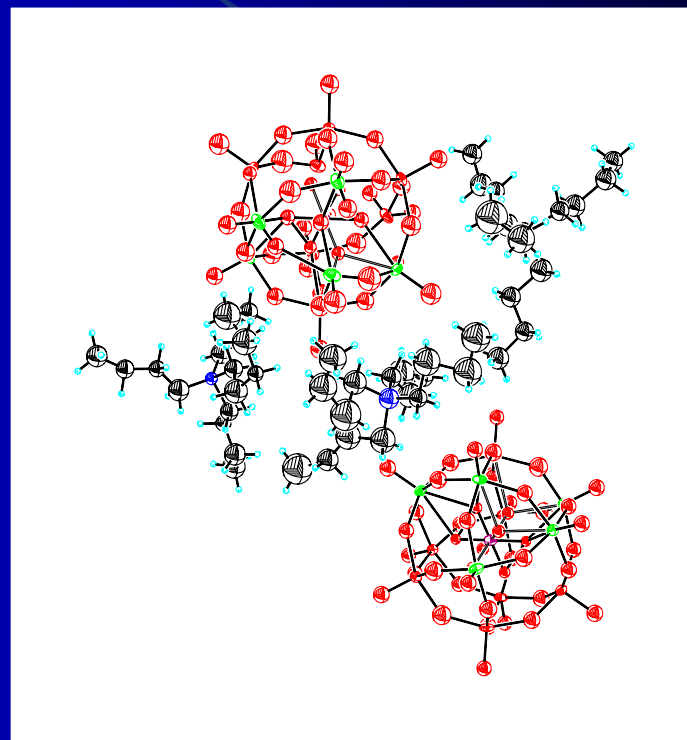
N.M. Okun, T.M. Anderson, C.L. Hill, *J. Am. Chem. Soc.* **2003**, 125, 3194.

N.M. Okun, T.M. Anderson, C.L. Hill, *J. Mol. Cat.* **2003**, 197, 283.

X-Ray structures

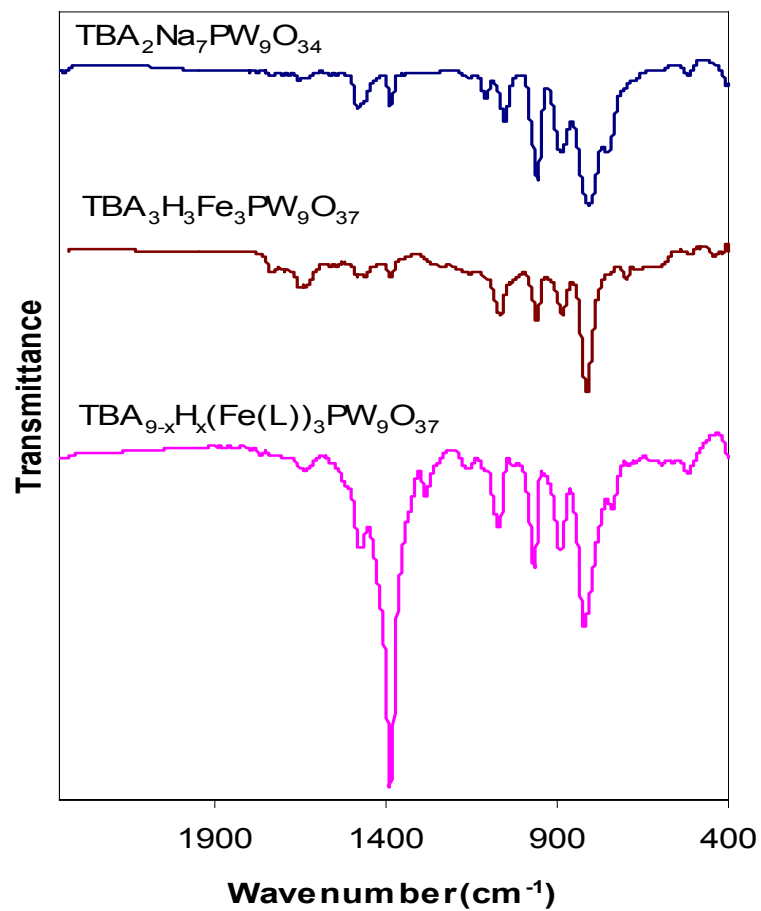


R = 4.19

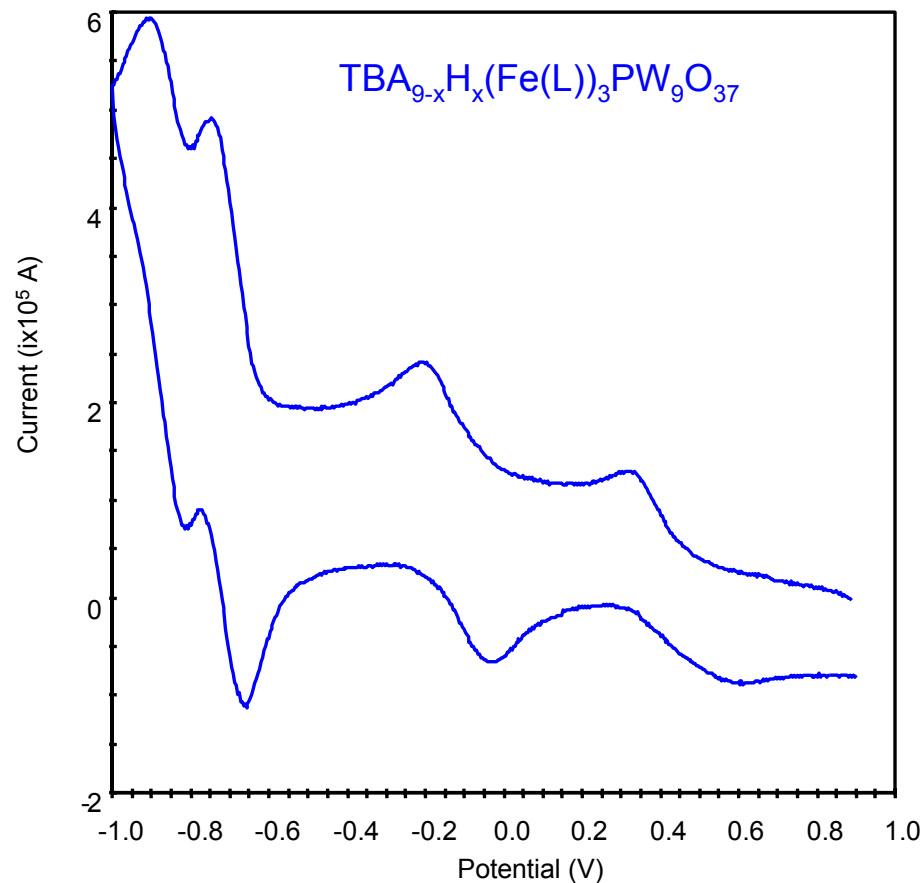
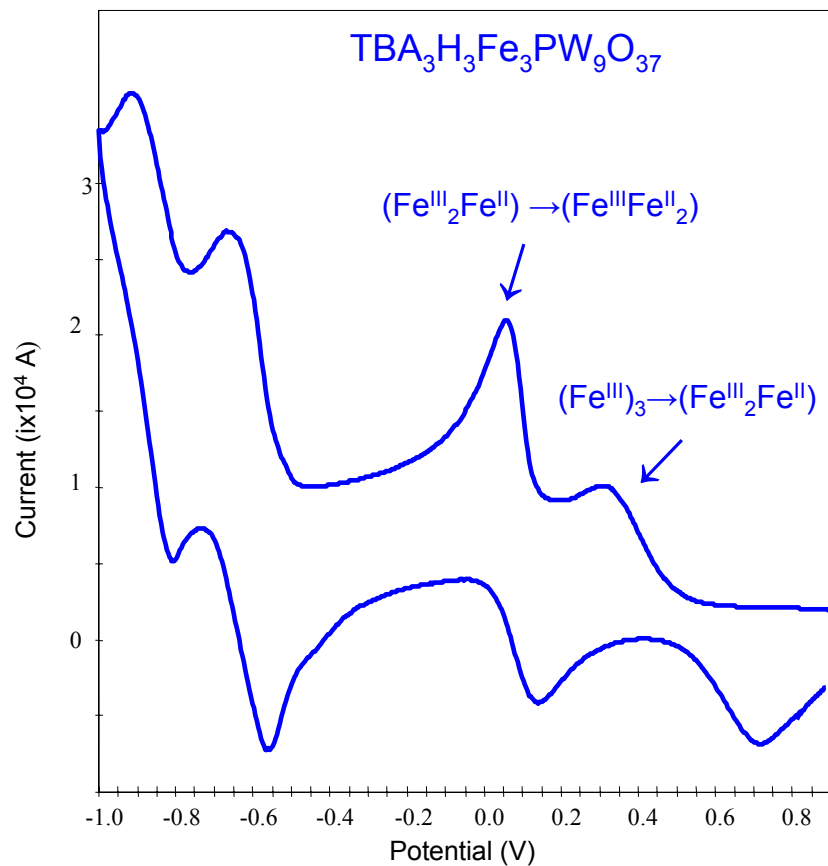


R = 9.16

IR Spectra

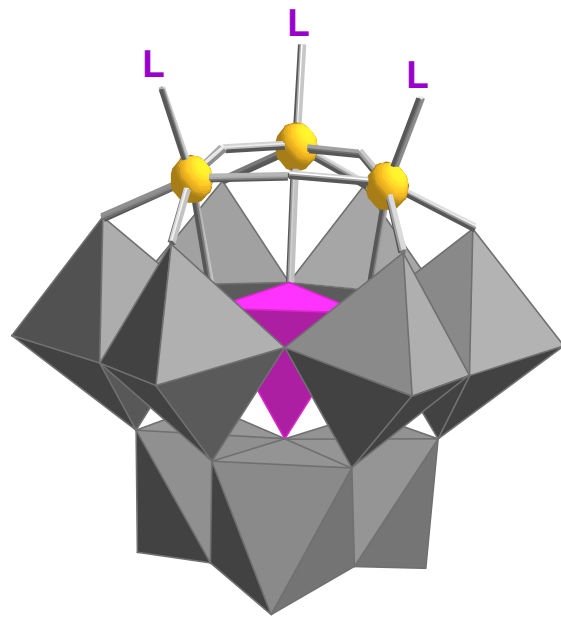
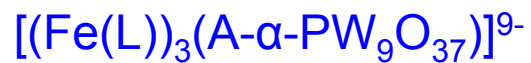


Redox potentials in solution (cyclic voltammetry)



Working electrode – glassy carbon; reference electrode – Ag/Ag^+ (0.1 M in acetonitrile); auxiliary electrode – Pt; scan rate 50 mV s^{-1} ; 23 $^{\circ}\text{C}$; supporting electrolyte – 0.1 M TBAClO_4 .

Proposed structure of the conjugate complex

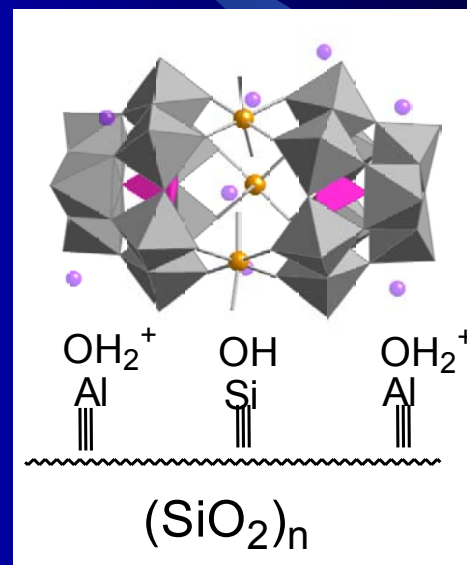
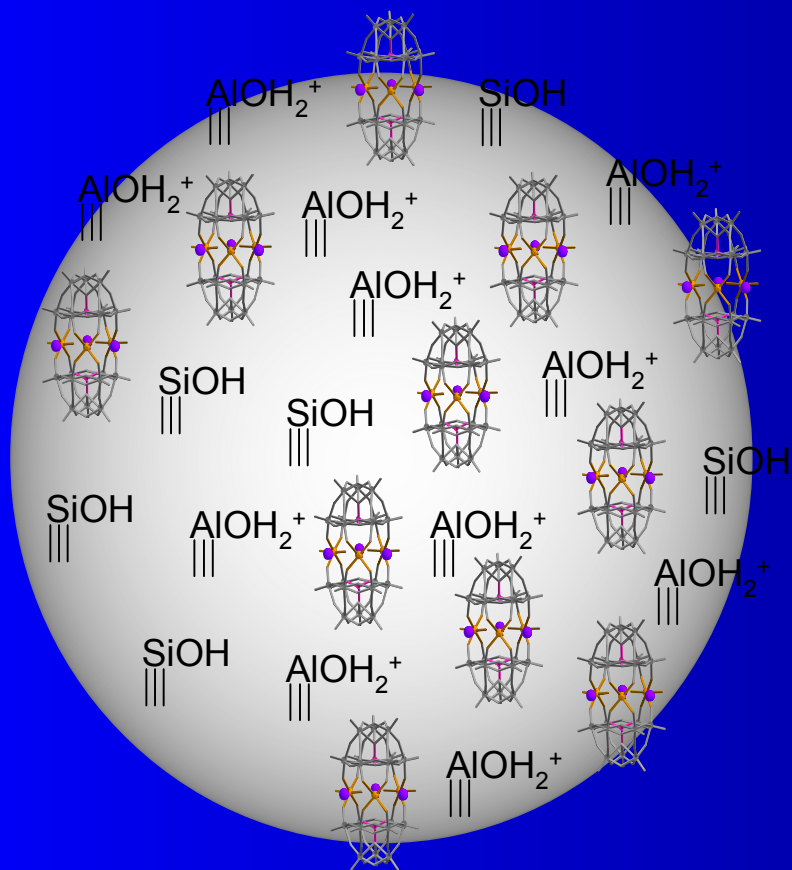


Aerobic sulfoxidation of 2-chloroethyl ethyl sulfide (CEES) in ~100% selectivity at 100% ultimate conversion catalysed by polyoxometalate (POM) and/or conjugate complex homogeneous catalysts at RT.^a

Catalyst	[catalyst] (mmol)	acidity ([OH]) ^b	aging time (days) ^c	TON ^d
TBA ₆ Fe ₃ PW ₉ O ₃₇	0.005	0.65	0	0
TBA ₆ Fe ₃ PW ₉ O ₃₇ + L	0.005	-	0	0
TBA _{9-x} H _x (Fe(L)) ₃ PW ₉ O ₃₇ (1)	0.005	-	0 (wet)	98
1	0.005	10.0	54	37

General conditions; ^a Acetonitrile solvent; [CEES]₀ = 0.875 mmol; RT; 1 atm of air;
^b[OH] = mmol of TBAOH/mmol POM used for titration; ^cdays of storage of POM on daylight; ^dtotal turnovers = moles of CEESO / moles of POM.

Illustration of the electrostatic association of $\{\text{K}_8[\text{Fe}_3(\text{A-}\alpha\text{-PW}_9\text{O}_{34})_2]\}^-$ monoanions with the cationic surfaces of the $(\text{Si}/\text{AlO}_2)^{n+}$ nanoparticles



N.M. Okun, T.M. Anderson, C.L. Hill, *J. Am. Chem. Soc.* **2003**, 125, 3194-3195.

Methods used for characterization of new catalysts

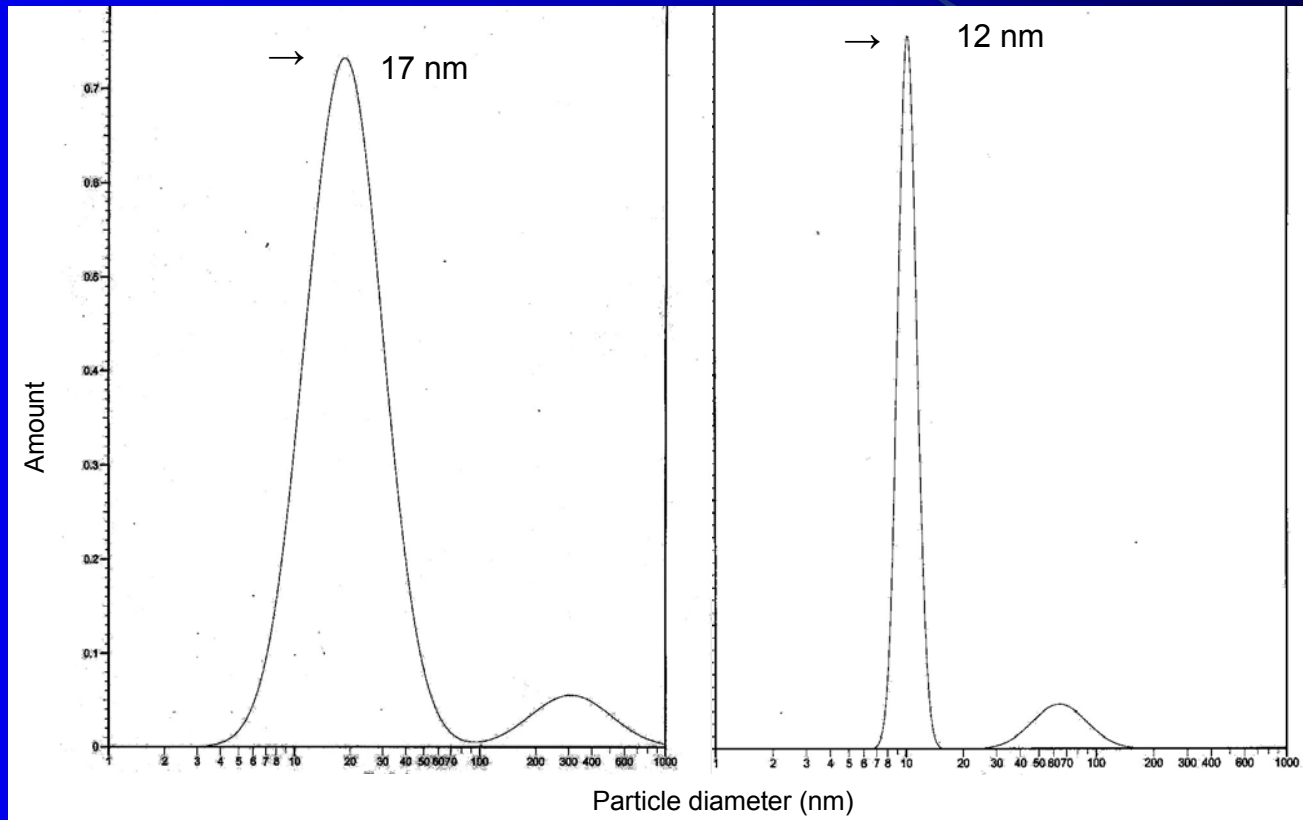
- Dynamic light scattering
- Elemental analysis, DRIFT, TGA, DSC
- Streaming potential
- Acid-base titration (PZC determination)
- Electron paramagnetic resonance
- Transmission electron microscopy
- cryo-High resolution scanning electron microscopy

Size distribution data by dynamic light scattering

$K_8[Fe_3(A-\alpha-PW_9O_{34})_2]/(Si/AlO_2)$

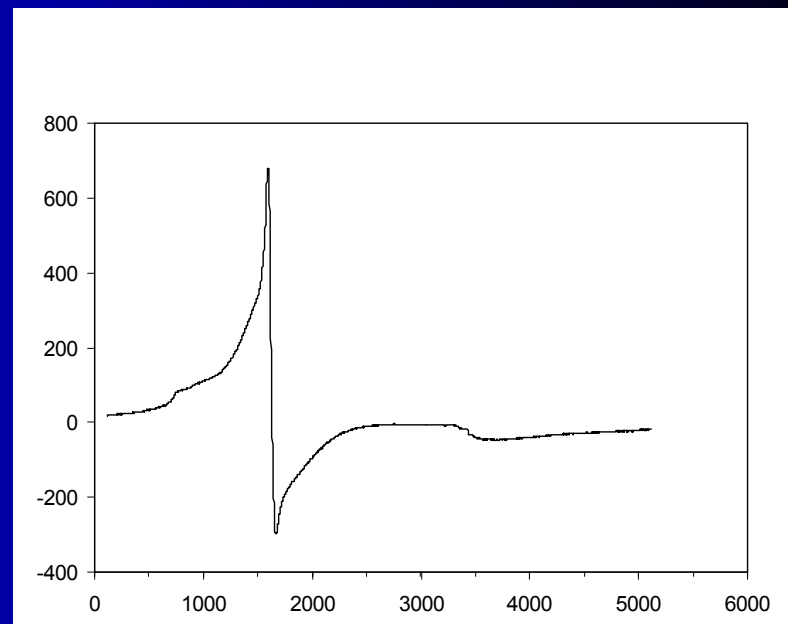
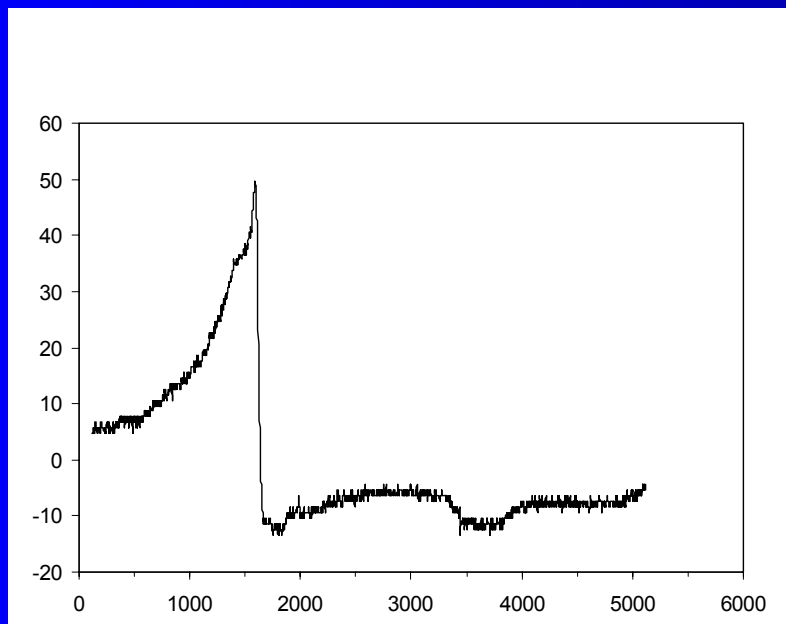
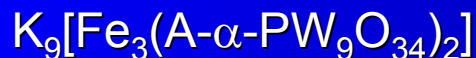
$(Si/AlO_2)Cl$

Bindzil CAT® (Akzo Nobel) nanoparticles.



General conditions: 25 °C; diluent water; angle 90.0°C; SDP (size distribution processor) settings Min 1.0 nm, Max 100 nm; Number of Bins 31.

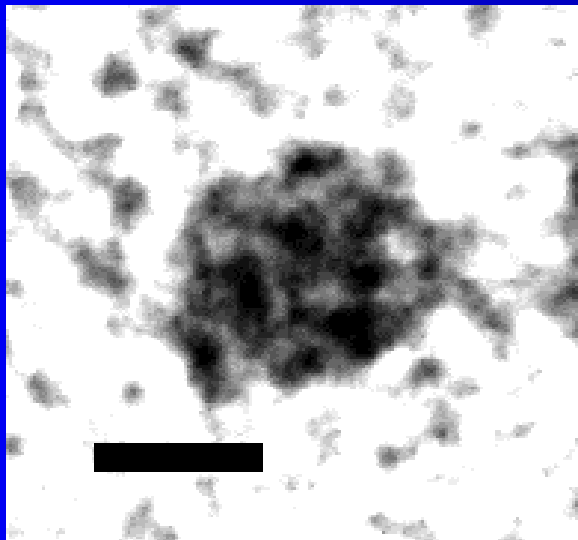
EPR spectra



Conditions. 0.2 mmol of $\text{K}_9[\text{Fe}_3(\text{A-}\alpha\text{-PW}_9\text{O}_{34})_2]$ free or bound to (Si/AlO_2) sonicated in 2 mL of light mineral oil. EPR spectra were recorded at 6 K using Brüker 200 spectrometer with a microwave frequency of 9.655 GHz and microwave power of 20 dB.

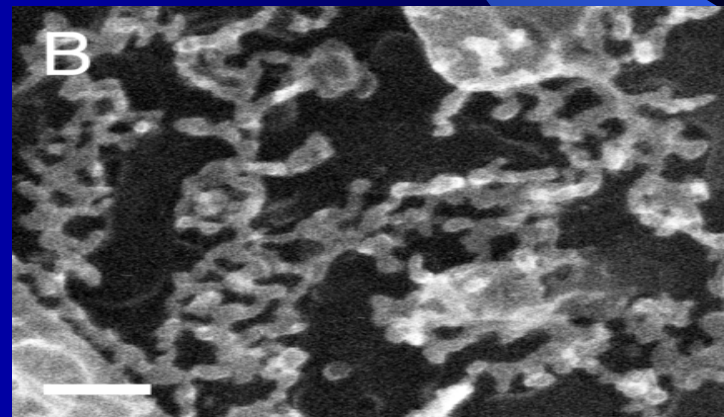
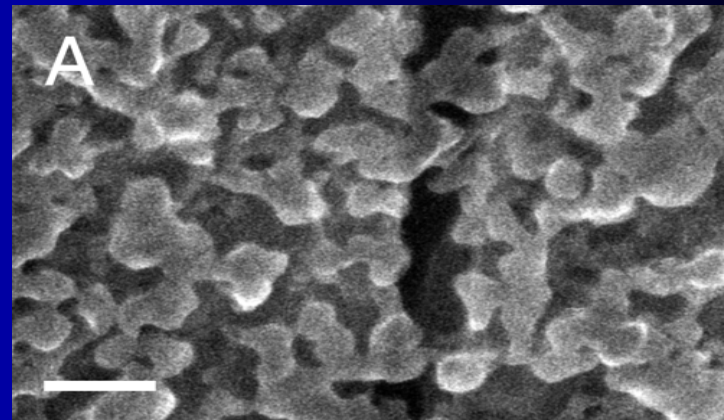
Conclusion: POM is structurally altered upon binding (the intensity of high-spin-ferric-like iron increased by an order of magnitude)

TEM and cryo-HRSEM



TEM image of an average-sized (~ 17 nm) particle of POM after catalysis. The sizing bar is 10 nm in length.

The dark spots of POM are more visible on the lighter background of the larger Si/AlO_2 nanoparticles.



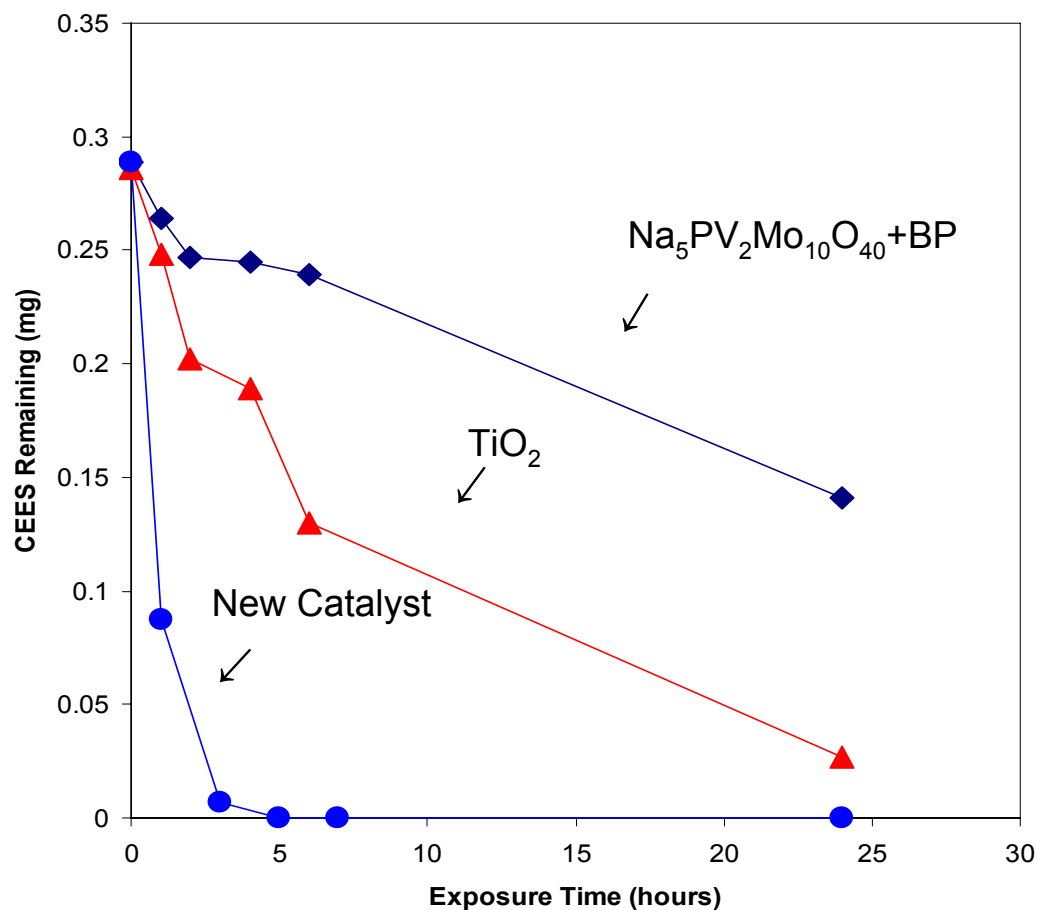
Cryo-HRSEM of cationic silica $((\text{Si}/\text{AlO}_2)\text{Cl})$ and $\text{K}_8[\text{Fe}_3(\text{A}-\alpha\text{-PW}_9\text{O}_{34})_2]/(\text{Si}/\text{AlO}_2)$. Both samples were aged 4 months prior to imaging.

Aerobic sulfoxidation of 2-chloroethyl ethyl sulfide (CEES) in 100% selectivity at 100% ultimate conversion catalysed by polyoxometalate (POM) and/or conjugate complex heterogeneous catalysts at RT.

Catalyst	POM (mmol)	TON		TOF	
		25 h	46 h	25 h	46 h
$\text{TBA}_{9-x}\text{H}_x(\text{FeL})_3\text{PW}_9\text{O}_{37}$ (1)	0.005	98	114	4.9	2.5
$(\text{Si}/\text{AlO}_2)\text{Cl}$ (2)	0	0	0	0	0
$\text{TBA}_{8-x}\text{1}/(\text{Si}/\text{AlO}_2)$ (100 °C)	0.001	23	136	1	3
$\text{TBA}_{8-x}\text{1}/(\text{Si}/\text{AlO}_2)$ (150 °C)	0.001	5.3	30	0.2	0.6
$(\text{TBA}_6\text{Fe}_3\text{PW}_9\text{O}_{37} + \text{L})/(\text{Si}/\text{AlO}_2)$	0.001	0	0	0	0

$[\text{CEES}]_0 = 0.875 \text{ mmol}$

Catalytic activity of our most recent catalyst (New Catalyst).
Data obtained at US Army Natick Soldier Center AMSSB-
RSS-MS(N)



Conclusion

- The most effective (selective and fast) catalysts yet for air oxidation of mustard (HD) have been developed – Fe-containing POMs with terminally coordinate redox-active ligand in solution or bound to cationic silica nanoparticles.
The “New Catalyst” will be reported only after patent is filed (next week).

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